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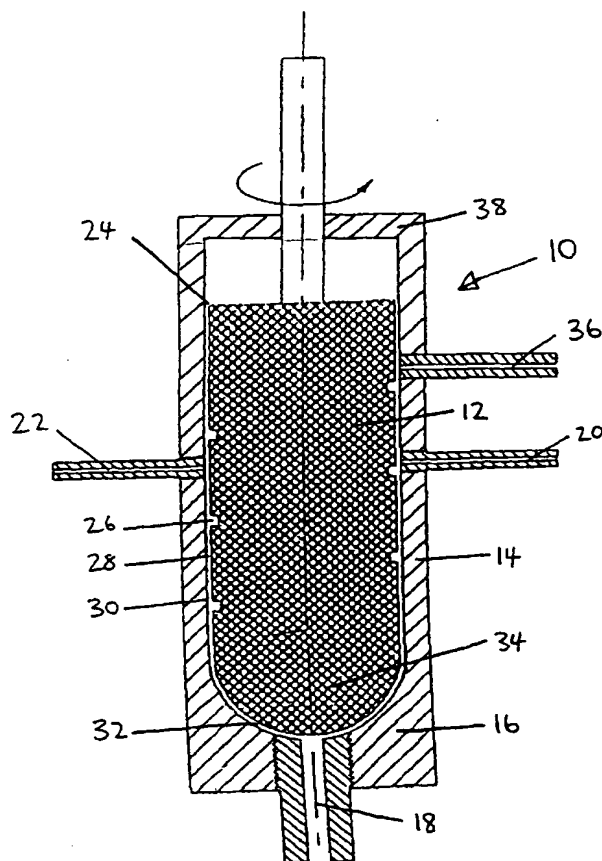
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(54) Title: LIQUID PHASE REACTOR



(57) Abstract: A liquid phase continuous reactor comprising a screw within a barrel, the screw and the barrel being relatively rotatable and defining a mixing zone therebetween, the barrel having at least one inlet for introduction of components for mixing into the barrel and an outlet for discharge of product from the barrel, the screw having at least one spiral groove whereby relative rotation of the screw and barrel is adapted to axially transport the components between the screw and the barrel while mixing the components and to extrude the product through the outlet, wherein the land surface area between the spiral groove forms at least 50 % of the surface area of the screw in the mixing zone.

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## LIQUID PHASE REACTOR

This invention relates to a liquid phase reactor. More specifically, the invention relates to a continuous flow reactor for liquid phase processing, for example to produce precursors for solid products and to mix multi-phase liquid systems. This invention also relates to a process for conducting liquid phase reactions in a reactor to produce, for example, precursors for solid products and to a process for mixing multi-phase liquid systems in a reactor.

Liquid phase processing such as wet chemistry processing can be performed in a reactor such as a batch reactor, continuous stirred tank reactor or plug flow reactor. Batch reactors allow reactants to react together in a vessel over a period of time. During the reaction, other reactants optionally may be added. The product formed is discharged at the end of the process. For batch reactors to be industrially useful they are often of large volume and consume large amounts of energy when high turbulent mixing is required.

Continuous stirred tank reactors operate continuously with out-flow being equal to total feed streams. Often the reactors are in series and, like batch reactors, are of a large total volume and require high turbulent mixing.

Plug flow reactors allow reactants to flow into the reactor without back-mixing. The rate of reaction is highest in the first part of the reactor where the concentrations of the reactants are highest. Plug flow reactors are more suitable for reactions of high reaction rates. However, the reactions can be difficult to follow and do not allow for compensation of times or conditions during production runs.

Extruders have been proposed for conducting reactions to produce plastics and other organic material. For example US Patent No. 5,266,256 describes a twin-screw extruder for the polymerisation of methyl methacrylate in which the residence time of the reactants in the extruder is increased.

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It has now been found in accordance with the invention that precursors for solid products can be prepared from reactants in the liquid phase in an extruder-type reactor. Reactors of the present invention can achieve high production rates with a reactor size significantly smaller than batch or continuously stirred tank reactors, provide better product of more uniform quality and reduce the fixed operation costs of performing wet chemistry reactions. Reactors of the present invention can also be used to effectively mix multi-phase liquid systems such as paints, inks and pharmaceuticals.

According to the present invention there is provided a liquid phase continuous reactor comprising a screw within a barrel, the screw and the barrel being relatively rotatable and defining a mixing zone therebetween, the barrel having at least one inlet for introduction of components for mixing into the barrel and an outlet for discharge of product from the barrel, the screw having at least one spiral groove whereby relative rotation of the screw and barrel is adapted to axially transport the components between the screw and the barrel while mixing the components and to extrude the product through the outlet, wherein the land surface area between the spiral groove forms at least 50% of the surface area of the screw in the mixing zone. Preferably, the turbulence imparted to the components during the mixing is at least about 25,000 Reynolds number (R), preferably from 25,000 to 100,000R.

The liquid phase reactor of the present invention is particularly suited for processing multi-phase liquids, but may be used for slurry mixing and/or homogenization, advantageously at rotational speeds sufficient to achieve high turbulence in the components in the reactor.

Thus, also according to the present invention there is provided a process for mixing or homogenizing components such as multi-phase liquids in a reactor in accordance with the invention which comprises introducing the components to the mixing zone through the one or more inlets, relatively rotating the screw and the barrel to produce the desired mixing and/or homogenizing while axially transporting the components between the screw and the barrel, and discharging the product through the outlet.

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In a preferred embodiment, the reactor of the present invention may also be used for conducting liquid phase reactions whereby the components introduced into and mixed in the reactor chemically react.

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Thus, further according to the present invention there is provided a process for performing liquid phase reactions in a reactor in accordance with the invention which comprises introducing the components to a reaction to the mixing zone through the one or more inlets, relatively rotating the screw and the barrel to mix the components, causing the mixed components to react  
10 to produce a product, and discharging the product through the outlet.

The invention also extends to products produced by the reaction process.

In a preferred embodiment the outlet of the reactor of the present invention is connected or  
15 connectable to the inlet or to one of the inlets for recycling product.

Preferably the surface area defined on the wall of the barrel by the spiral groove is substantially smaller than the overall surface area defined on the wall of the barrel in the mixing zone by the screw.

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The volume of the mixing zone of the reactor is the sum of the annular volumetric clearance between the lands of the screw and the wall of the barrel (the clearance volume) and the volume of the spiral groove (the groove volume). Normally, the mixing zone will be considered to extend axially between the at least one inlet and the discharge outlet. Preferably, the groove  
25 volume will be as small as possible while still effective to transport the mixing/reaction components and/or product through the mixing zone. However, because of the preferred small depth of the clearance volume, the groove volume is likely to comprise at least 50% of the volume of the mixing zone. The maximum ratio of the groove volume to the clearance volume is preferably about 5:1, more preferably about 3:1.

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Preferably the volume of the groove is substantially smaller than the overall volume of the screw, for example in the range 1:10 to 1:50. In a laboratory scale embodiment of the reactor, the reactor screw may have a radius of about 15mm, the spiral groove may have a depth of about 1-3mm, the clearance volume may have a depth of about 0.01 to 3mm, preferably 0.05 to 0.5 mm, and the overall mixing zone may have a volume in the range of about 0.5 to 10cm<sup>3</sup>. As a result of the relatively small groove volume and the narrow clearance volume, the reactor is able to continuously produce high quality and uniform slurry product. A grinding action of solids in the components or product in the clearance volume greatly assists in achieving a uniform product.

It will be understood that the effective volume, depth, pitch, and length of the spiral groove(s) and the geometry of the screw in general determine process parameters such as residence time and turbulence which influence the product quality and production rate. These aspects of the reactor may need to be optimised and adapted to the critical parameters of the mixing performed in the reactor.

Advantageously, the discharge outlet opens to the barrel interior on the axis of the barrel, and preferably the clearance volume is rounded, for example part-spherical, between cylindrical portions of the screw and barrel wall and the discharge outlet.

The reactor can be operated in a vertical position, horizontal position or on an incline. Preferably the reactor is operated in the vertical position with the discharge outlet at the lowermost end, as gravitational forces beneficially influence sealing and mass transport. The screw may rotate at from about 100 to about 10,000 rpm, preferably from 500 to 2,000 rpm, to achieve the desired turbulent mixing. The preferred rotational speed is less than that required in large batch reactors (typically more than 2,000 rpm) to achieve a similar degree of high turbulent mixing. This helps to reduce the fixed operating costs of the reactor of the present invention.

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- 5 -

The effective transportation volume or mixing zone of the present reactor can be significantly less than that of batch reactors, leading to substantial advantage when relatively small quantities of product are required. Typically, the production rate (product throughput) using reactor of the present invention is from 0.25 to 0.75 kg/h, preferably about 0.5 kg/h.

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Mixing may be performed at ambient or elevated temperatures.

In the reaction process, the individual components for reaction may be introduced into the barrel through respective inlets. Solvents, catalysts, moderators and/or carriers may be added to control or aid the mixing and reaction.

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The residence time in the reactor is usually less than in a conventional batch reactor, requiring the rate of reaction to be rapid. However where incomplete or insufficient reaction has been achieved, the product obtained may be fed back into the reactor for a second or subsequent pass.

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The required recycle rate is largely determined by the reaction rate.

The temperature at which the components are reacted in the reactor may be from ambient up to 500°C or more depending on the components, their concentrations and other factors. Heating may be achieved by reaction, by heating one or more of the reaction components and/or by heating the barrel and/or screw. Optionally, cooling of the reactor may be provided.

20

The reactor of the present invention can produce a slurry product, including a slurry precursor of a solid product. The product obtained may be a precipitate, co-precipitate or sol-gel, more preferably a precursor powder of uniform consistency and high quality. The product can be inorganic, organic or a mixture thereof.

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In a preferred embodiment, the reactor of the present invention is used for powder precipitation. Typical reactions that may be performed in the reactor are precipitations and co-precipitations. These and other reactions can produce precursor solid products such as insoluble inorganic precursors of simple oxides, multi-component oxides, mixed oxides, or mixtures thereof having

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homogeneity and high dispersion. Such reaction products can lead to uniform, highly dispersed and high reactivity powders for further processing (eg. sintering to ceramic parts).

Embodiments of the present invention will now be described by way of example only with  
5 reference to the following Examples and the accompanying drawing. The Examples and drawing are not to be construed as limiting the invention in any way.

The drawing is a part-sectional representation of a laboratory-scale annular reactor. The drawing illustrates reactor 10 having a screw 12 rotatably supported in a barrel or cylinder 14.

The axis of rotation of screw 12 is vertical. The screw has a rounded, part-spherical bottom end  
10 34, and the cylinder 14 has a plugged, correspondingly-shaped bottom end 16 with an outlet 18 on the axis of rotation, and a closed top end 38. Components for reaction are fed into the reactor 10 through inlets 20 and 22, and recycled material from the discharge outlet 18 may be introduced through inlet 36. The inlets 20 and 22 are opposite one another part-way down the axial length of the cylinder and the inlet 36 for recycled material is disposed between the top 24  
15 of the screw 12 and the inlets 20 and 22.

A cylindrical portion of the screw is provided with a surface spiral groove 26 for axially transporting and turbulently mixing the components as the screw is rotated. A clearance volume  
20 28 and 32 between the screw 12 and the cylinder 14 combines with the groove volume to define a mixing zone, with grinding of solids in the clearance volume greatly assisting the formation of homogenous product. In the illustrated reactor 10, the clearance volume has a depth of about 0.1mm. The volume and depth of the groove 26 is substantially less than the volume and radius, respectively, of the screw 12, the groove having a depth of about 2mm while the screw has a radius of about 15mm. The surface area defined by the groove 26 on the internal wall 30 of the  
25 cylinder 14 is substantially less than the land area between the portions of the groove and forms less than 10% of the overall surface area defined by the screw 12 on the internal wall 30 of the cylinder 14. The ratio of the volume of the groove 26 and the clearance volume 28 is about 2:1. The volume of the reaction zone of the laboratory scale reactor 10 as illustrated is about 1.5 cm<sup>3</sup>. A production scale reactor may be substantially larger.

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Example 1:

- 5 A stabilised zirconia powder of the composition 8 mol% yttria-zirconia was co-precipitated from a defined mixture of yttrium and zirconium nitrate and ammonia solution in the continuous flow reactor 10. The reaction produced a very homogenous precursor slurry at a rotation speed of 750 rpm and at a production rate of about 0.5 kg/h. The slurry was filtered and the resulting powder precursor calcined at 750°C to achieve the product powder.

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For comparison, the precipitation was also carried out at the same ratio in a conventional batch reactor at stirring rates of 2,000 - 3,000 rpm. The results are summarised in Table 1.

**Table 1**

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	Continuous flow Reactor	Batch reactor
Effective volume	1.5 cm <sup>3</sup>	60 L
Residence time	1 sec	4 h
Stir speed	750 rpm	>2000 rpm
Power	0.1 KW	2.5 KW
Production Rate	0.5 kg/h	0.17 kg/h
Quality of product	Uniform, highly sinterable powder	Some inhomogeneity, low sintering reactivity

Example 2:

A perovskite of the composition  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  was produced by co-precipitation from a mixed

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lanthanum-, strontium-, manganese-nitrate solution under the conditions outlined in Example 1. After filtration, drying and calcination at 800°C a homogenous single phase perovskite powder was obtained. Again very high stirring rates (high energy consumption) was necessary in a conventional batch precipitator to achieve similar powder quality.

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Other precipitations performed with the reactor 10 included scandia-zirconia, and other perovskites such as Lanthanum-strontium-chromite, and in all cases very uniform powder products were obtained.

10 Example 3:

The reactor 10 is also useful for mixing/homogenization/dilution of slurries such as paints or inks. A slurry containing 50 wt% solids (titania powder) was passed through the reactor 10 with a measured amount of water to achieve 30% solids content. A very uniform slurry was obtained at a stirring rate of 1000 rpm.

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Throughout this specification, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

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Those skilled in the art would appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more said steps or features.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A liquid phase continuous reactor comprising a screw within a barrel, the screw and the barrel being relatively rotatable and defining a mixing zone therebetween, the barrel having at least one inlet for introduction of components for mixing into the barrel and an outlet for discharge of product from the barrel, the screw having at least one spiral groove whereby relative rotation of the screw and barrel is adapted to axially transport the components between the screw and the barrel while mixing the components and to extrude the product through the outlet, wherein the land surface area between the spiral groove forms at least 50% of the surface area of the screw in the mixing zone.
2. A reactor according to claim 1, which imparts a turbulence to the components during mixing of at least about 25,000 Reynolds number (R).
3. A reactor according to claim 2, wherein the turbulence is from 25,000 to 100,000R.
4. A reactor according to any one of the preceding claims, wherein the outlet of the reactor is connected or connectable to the inlet or to one of the inlets for recycling product.
5. A reactor according to any one of the preceding claims, wherein the surface area defined on the wall of the barrel by the spiral groove is substantially smaller than the overall surface area defined on the wall of the barrel in the mixing zone by the screw.
6. A reactor according to any one of the preceding claims, wherein the volume of the spiral groove (the groove volume) is as small as possible while still effective to transport the components and/or product through the mixing zone.
7. A reactor according to claim 6, wherein the groove volume comprises at least 50% of the volume of the mixing zone, the mixing zone being the sum of the annular volumetric clearance between the lands of the screw and the wall of the barrel (the clearance volume) and

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the groove volume.

8. A reactor according to claim 7, wherein the maximum ratio of the groove volume to the clearance volume is about 5:1

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9. A reactor according to any one of the preceding claims, wherein volume of the spiral groove is substantially smaller than the overall volume of the screw.

10. A reactor according to claim 9, wherein the ratio of the volume of the spiral groove to the overall volume of the screw is from 1:10 to 1:50.

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11. A reactor according to any one of the preceding claims, wherein the discharge outlet opens to the barrel interior on the axis of the barrel.

12. A reactor according to any one of the preceding claims which is provided in the vertical position with the discharge outlet at the lowermost end.

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13. A process for mixing or homogenizing components using a reactor as claimed in any one of claims 1 to 12, which process comprises introducing the components to the mixing zone through the at least one inlet, relatively rotating the screw and the barrel to produce the desired mixing and/or homogenizing while axially transporting the components between the screw and the barrel, and discharging the product through the outlet.

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14. A process for performing a liquid phase reaction in a reactor as claimed in any one of claims 1 to 12, which process comprises introducing the components for a reaction to the mixing zone through the at least one inlet, relatively rotating the screw and the barrel to mix the components, allowing the mixed components to react to produce a product, and discharging product through the outlet.

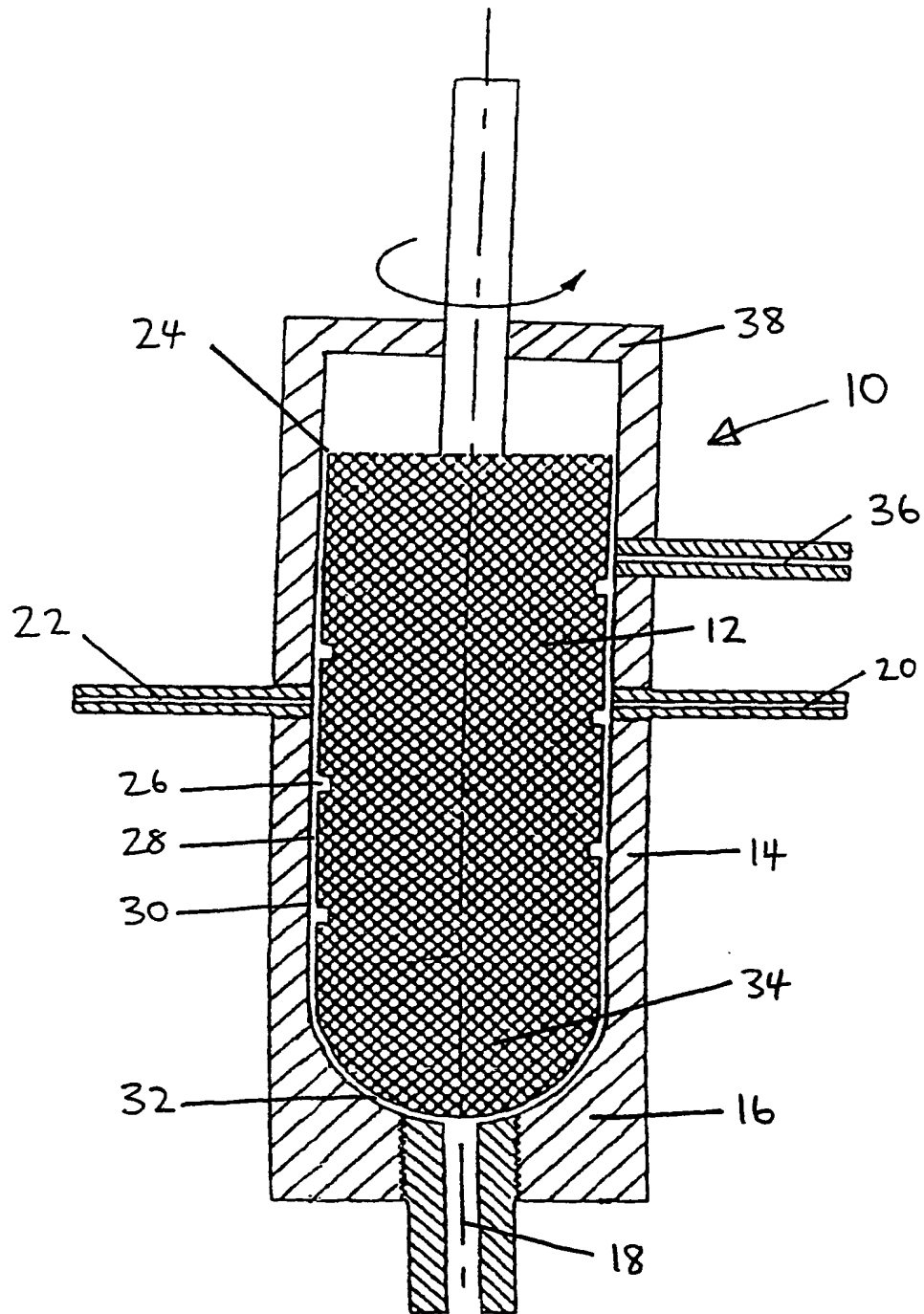
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15. A product produced by the process claimed in claim 13 or 14.

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16. Use of a reactor as claimed in any one of claims 1 to 12 for powder precipitation.
17. Use according to claim 16 to produce insoluble inorganic precursors of simple oxides,  
5 multi-component oxides, mixed oxides, or mixtures thereof having homogeneity and high dispersion.



**FIGURE 1**

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00338

**A. CLASSIFICATION OF SUBJECT MATTER**Int. Cl. <sup>7</sup>: B01J 19/28

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC B01J 19/28, 19/20, 8/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT IPC B01J 19/28, 19/20, 8/10 AND KEYWORDS (screw, helix, helical, spiral, groove, land) and like terms

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0090148 A (Nukem GmbH) 5 October 1983 (05.10.83) (see page 4, line 1 - page 6, line 28 and figure II)	1 - 17
PA	WO 0126804 A (Der Grune Punkt - Duales System Deutschland AG) 19 April 2001 (19.04.01) (see page, line 22 - page 6, line 26 and figure 1 - 2)	1 - 17

☐ Further documents are listed in the continuation of Box C
 ☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU02/00338**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	200126804	AU	200077723	DE	19949288
EP	90148	CA	1190383	DE	3205569
		ES	8403154	JP	58156340
					ES 519130
					END OF ANNEX